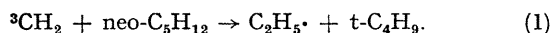


Triplet Methylene; A New Reaction

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AMONG the products of the reaction of triplet methylene (produced by the mercury-photosensitized decomposition of keten) with neopentane¹ are compounds which show the presence of t-butyl radicals in the system (isobutene and 2,2,5,5-tetramethylpentane), arising from the reactions of the t-butyl radical with the neopentyl radical (which is present in relatively high concentration). The formation of t-butyl, may be considered as an abstraction



of a methyl group or as a displacement on a saturated carbon atom. The only precedent for such a displacement reaction is²



In this case it is not known whether the reaction is due to singlet or triplet methylene, but in any event the unusual bonding in this highly strained bicyclic-system makes it a poor analogue. In most studies of methylene with paraffins the occurrence of this displacement reaction cannot be distinguished on the basis of product analyses from other known reaction pathways. It is also possible that reaction (1) or its equivalent has not been previously noted because it may require the triplet methylene to be vibrationally excited, which would eliminate it as a possibility when high dilutions of inert gases are used.

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¹ Preceding Communication.

² W. von E. Doering and J. F. Coburn, *Tetrahedron Letters*, 1965, 991.